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Surface properties of carbon fibres modified by electrodeposition of polyamic acid

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The objective of this work is to study the surface property changes of carbon fibres resulting from the electrodeposition of polyamic acid. Unsized but surface oxidized carbon fibres were successfully coated with polyamic acid by non-aqueous electrodeposition. The surface property changes due to the electrodeposition were studied by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (*FT*i.r.), dynamic contact angle analysis (DCA) and thermogravimetric analysis (t.g.a.). The SEM analysis showed smooth, continuous and thick polyamic acid coatings. The electrodeposition of polyamic acid on graphite fibres did not result in a self-limiting film growth. *FT*i.r. spectroscopy confirmed that the electrodeposited coatings possessed the same chemical structure and functionality as the bulk polymer, indicating that electrodeposition did not result in alteration of the polymer structure. The surface energy of the coated T650/35 and T-300 fibres was found to be about 15% and 20% respectively, lower than that of the uncoated fibres. T.g.a study showed that the cured polyimide has excellent thermal stability up to 540°C. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyamic acid; polyimide; carbon fibres; electrodeposition; fibre modification; surface energy; adhesion)

Introduction

The nature of the surface of carbon fibres is of considerable relevance to the performance of fibrous composites. Even though carbon fibres possess numerous attractive properties, they are poorly wetted by the polymer matrix, resulting in low interlaminar shear strength of the composite.

Tremendous efforts have been devoted so far on the modification of carbon fibre surface[1-9]. These efforts have been focused on three areas: surface treatment, surface coating and a combination of both. The purpose of surface treatment is to enhance the wettability of carbon fibres and their adhesion to the polymer matrix. However, one of the disadvantages of this approach is that improvements in the interlaminar shear strength are attained at the expense of reduced impact strength. The strategy of surface coating is to insert a suitable polymer interlayer between the carbon fibres and the polymer matrix and to use its properties to control the level of fibre/matrix adhesion[10-17].

In this paper the property changes that occur in carbon fibres as a result of electrodeposition of polyamic acid are reported. By adopting the electrodeposition process as a surface coating technique, it is easy to control the thickness and functionality of the coatings through selective control of processing parameters (solvent/precipitant ratio, acid/base ratio, solid content, current density, pH of the medium). In addition, a complete uniform polymer coating can be formed on each individual fibre filament in a fibre bundle of about 3–12 k filaments.

Experimental

Materials. Unsized but surface oxidized Thornel T-650/35 and T-300 carbon fibres, from Amoco Performance Products, Inc., were used in this study. The PI2545 polyamic acid, which was prepared from pyromellitic dianhydride (PMDA) and 4,4-oxydianiline (ODA), was obtained from E. I. Dupont de Nemours & Co. The polyamic acid was dissolved in *N*-methyl-2-pyrrolidone (NMP) with a solid content of 13.4%. Reagent grade dimethylformamide (DMF), triethylamine (TEA), methanol, hexadecane and formamide were purchased from Fisher Scientific Co. and Aldrich Chemical Co. and used as received.

Electrodeposition. A single carbon fibre tow was wound onto an H-shaped polypropylene frame which was covered at both ends with aluminium foil to increase conductivity. The aluminium foil was cleaned of grease and dirt with methanol and then left in the hood for 30 min before it was wrapped on both ends of the frame. A schematic representation of electrodeposition of polyimide is shown in *Figure 1*. The frame bearing the single carbon fibre bundle was connected to the positive terminal of the potentiostat and served as the anode. The cathode was made up of two stainless steel plates ($153 \times 38 \times 1\,\mathrm{mm}^3$). Electrodeposition was carried out chronopotentiometrically. A constant current of 50 mA was applied to the electrochemical cell for 1 min. Emulsion for the electrodeposition was composed of the following: a solid content of 1 wt%, precipitant/solvent, P/S, ratio of 3.5/1.0, and TEA/COOH mole ratio of 1/1. Methanol and dimethylformamide were used as the precipitant and the solvent, respectively.

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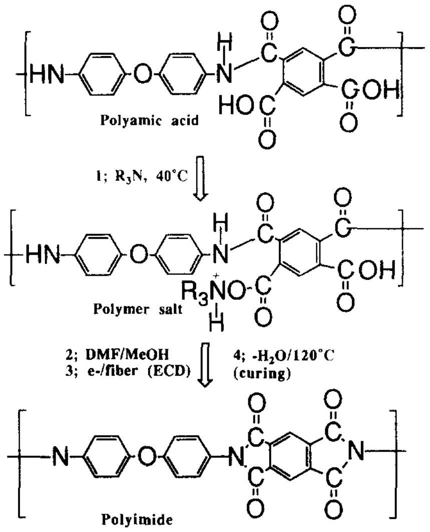

Figure 1 Schematic representation of electrodeposition of polyimide

The coated fibres were withdrawn from the solution immediately after electrodeposition and left to dry in the hood overnight. The coating was finally dried to constant weight at 100°C.

Scanning electron microscopy (SEM). The surface morphology of the coated and uncoated single fibres was studied by using the scanning electron microscope (Stereoscan 90, Cambridge Inc.). The samples were shadowed with gold to enhance their conductivity and thus achieve good resolution of the images.

*Fourier transform infrared spectroscopy (*FT*i.r.).* *FT*i.r. spectra were obtained by using a Perkin-Elmer 1800 Fourier transform infrared spectrometer. The spectra were taken at a resolution of 4 cm^{-1} for 10 cycles from 4000 cm^{-1} to 450 cm^{-1}. The *FT*i.r. samples were prepared by placing a polyamic acid solution (with DMF as the solvent) directly on a KBr crystal disc (PKBr 25.0 × 4, OPTOVAC, EM Industries, Inc.), followed by drying in a vacuum oven between 80 and 85°C for 15 min to remove the solvent. The coated polyamic acid film was extracted in DMF for 24 h and the infrared spectra were obtained by following the procedure described above. The cured polyimide samples were prepared first by placing polyamic acid solution on the KBr crystal disc as described above, followed by curing in a vacuum oven at about 200°C for 1 h.

Dynamic contact angle analysis (DCA). All the DCA measurements were carried out with the Cahn's DCA-322 system, which is based on the Wilhemy technique. The uncoated and coated single fibres were first cut to about 15–20 mm in length. Tape was placed at one end to increase the clamping area. The fibre was then hung on the electronic balance through a clamp. The DCA analysis was performed at a speed of 20 μm s^{-1}, with hexadecane, deionized water and formamide, respectively, as the wetting medium. Five samples were tested for each category and the results averaged.

Thermal gravimetric analysis (t.g.a.). T.g.a. was performed on a PL-Thermal STA 1500H thermogravimetric analyser. The measurements were carried out in a nitrogen atmosphere (flow rate ~26 cm^3 min^{-1}) at a heating rate of 10°C min^{-1}.

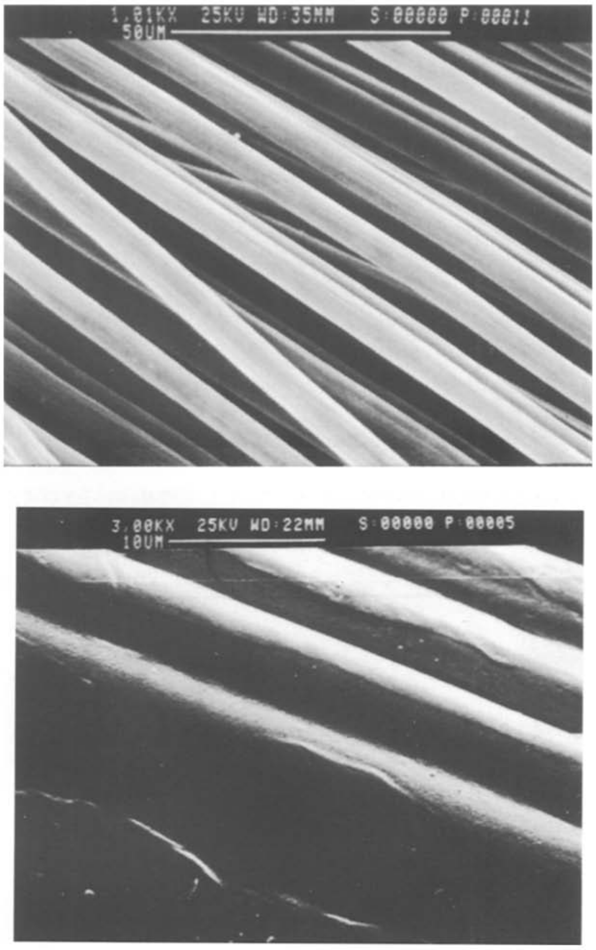

Figure 2 SEM micrographs of T-650/35 carbon fibres before (top) and after (bottom) electrodeposition of polyimide

Results and discussion

SEM microscopy. *Figure 2* shows the SEM micrographs of a fibre bundle before (top) and after (bottom) electrodeposition. The surface of the coated fibres appears quite smooth. Note the presence of longitudinal striations on the uncoated fibres (*Figure 2*, top). These striations occur during the manufacture (spinning and surface oxidation) of the fibres. It was reported that surface treatments increased the fibre surface roughness by pitting and increased longitudinal striations[1].

Figure 3 shows the surface morphology of a single fibre after electrodeposition. The individual fibre filament is effectively covered by uniform polymer film. As the polymer film is formed, the increased electrical resistance of the coating directs further film formation to uncoated areas which are more conductive, enabling a uniform film to be built up free of pinholes. Note that the diameter of the single non-coated fibre increased from about 7 μm to about 100 μm for the coated fibre. This observation suggests that the polymer coating formed is not completely insulating so that film formation is not self-limiting. Alvino *et al.*[18] obtained similar results. They suggested that the freshly deposited polyamic acid is highly swollen, porous and conductive. This film property permits the application of specific amounts of polymer coating directly onto a conductive fibre preform. This is especially useful when composites with a high resin volume-fraction are desirable. Note that it is

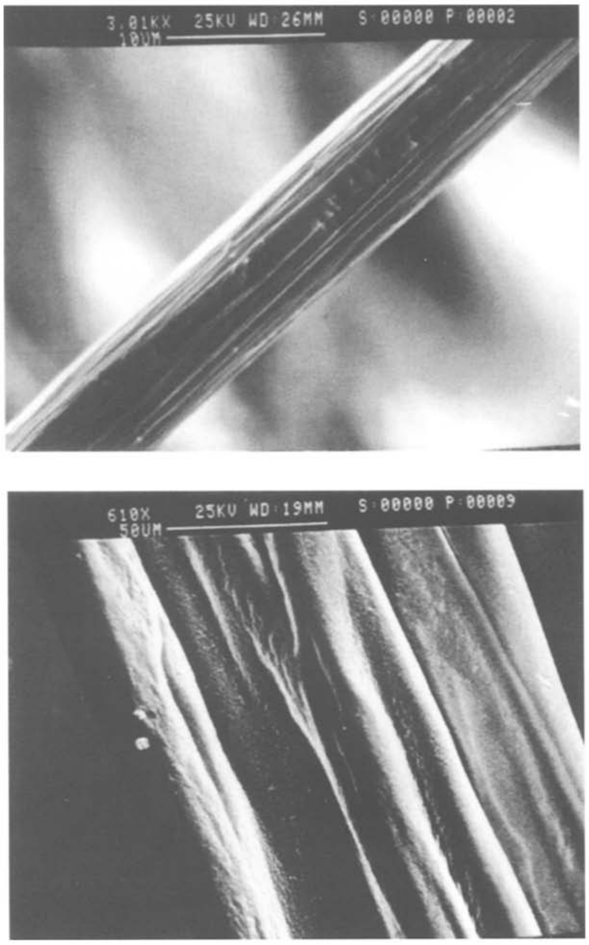

Figure 3 SEM micrograph of uncoated (top) and coated (bottom) single fibre (T-650/35)

not easy to fabricate high resin content prepreg from the wet and hot melting techniques.

*Fourier transform infrared spectroscopy (*FT*i.r.).* *FT*i.r. spectra of the polyamic acid before and after electrodeposition are compared in *Figure 4*. Similar absorption bands were observed for both samples. Bands near 1720 and 1304 cm^{-1} were assigned to the vibrational modes of acid groups. Bands near 1660, 1540 and 1406 cm^{-1} were assigned to the vibrational modes of amide groups. The bulk polyamic acid and the electrodeposited polymer film were cured at 200°C for 1 h.

Figure 5 compares the *FT*i.r. spectra of the cured products. All the bands related to the acid and amide groups disappeared after curing. However, the characteristic absorption bands of the imide groups near 1778, 1723, 1375, 1115 and 723 cm^{-1} were observed in the *FT*i.r. spectra of the cured samples. The structure of the electrocoated polyamic acid and the corresponding polyimide was similar to that of the bulk polyamic acid and the corresponding polyimide, respectively. Thus electrodeposition did not result in alteration of the polymer structure.

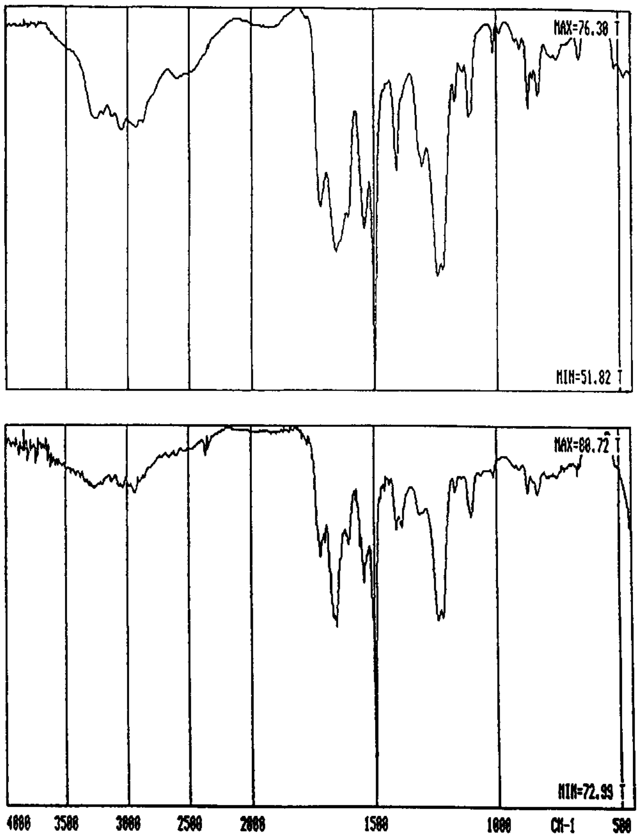

Figure 4 *FT*i.r. spectra of polyamic acid before (top) and after (bottom) electrodeposition

Surface energy analysis. The perimeters of the coated and non-coated single fibres were determined by the dynamic contact angle analyser (DCA) (*Tables 1–4*). Hexadecane was the wetting medium used, being preferred because of its low surface tension, ~21 mJ m^{-2}, and its ability to spread (to satisfy the requirement of zero contact angle). The perimeter was calculated from the equation

$$P = \frac{F}{\gamma \cos \theta}$$

where P is the perimeter of the fibre, F is the force measured by the microbalance, γ is the surface tension for a standard liquid (e.g. for hexadecane $\gamma \simeq 21$ mJ m^{-2}) and θ is the contact angle of the liquid against the fibre. (For hexadecane against the carbon fibre, $\theta = 0$ and $\cos \theta \simeq 1$.)

The results of the perimeter measurements on non-coated T-650/35 and T-300 single fibres are presented in *Tables 1* and *2* respectively. These results are very consistent. The fibre diameter, calculated from the perimeter, is also listed in *Tables 1* and *2*. The diameter of a single fibre, obtained by using this approach, is about 5.7 μm, which is slightly lower than the 6.8 μm and 7.0 μm reported for the T-650/35 and T-300 fibres respectively by Amoco Performance Products, Inc. This is probably due to the fact that the carbon fibre is not completely wetted by hexadecane, so that the calculated perimeter is lower than the measured value.

The perimeters of the coated T-650/35 and T-300 fibres are shown in *Tables 3* and *4* respectively. The fibres were electrocoated by passing an electric current of 50 mA through the electrodeposition cell for 1 min, using an emulsion composition with a P/S ratio of 3.5/1, solid content of 1.0 wt%, and TEA/COOH mole ratio of 1.0/1.0. The diameter of the coated fibres, calculated from the perimeter, is also listed in *Tables 3* and *4*. The thickness of the coatings was in the range of

50–100 μm. These results were confirmed by SEM micrographs (*Figure 3*). However, the thickness of the coatings varied for most samples. This may be because the film growth was not self-limiting.

Surface energy measurement for coated and non-coated single fibres. The total surface energy (γ^T), as well as the dispersive (γ^D) and polar (γ^P) components of the coated and non-coated single fibre energy, were determined by using the harmonic and geometric two-liquid methods in the solid surface modules of Cahn's DCA application software. A detailed description is given by Wu[19] and by Owens and Wendt[20].

The surface energies of the non-coated T-650/35 and T-300 single fibres, determined by the harmonic and geometric mean methods, are summarized in *Tables 1* and *2* respectively. The corresponding values for the electrocoated single fibres are summarized in *Tables 3* and *4* respectively. The total surface energy, γ^T, for the same material determined by both methods is very comparable. The harmonic methods gave higher γ^P values than the geometric method.

The average values of γ^P, γ^D and γ^T for the non-coated T-650/35 and T-300 single fibres are in the range of those for surface treated carbon fibres. The difference in γ^T between the T-650/35 and T-300 single fibres can be traced to their γ^P values. The average value of γ^P for the non-coated T-300 fibre is higher than that for the non-coated T-650/35 fibre, indicating that the T-300 fibre may have more polar chemical functional groups on its

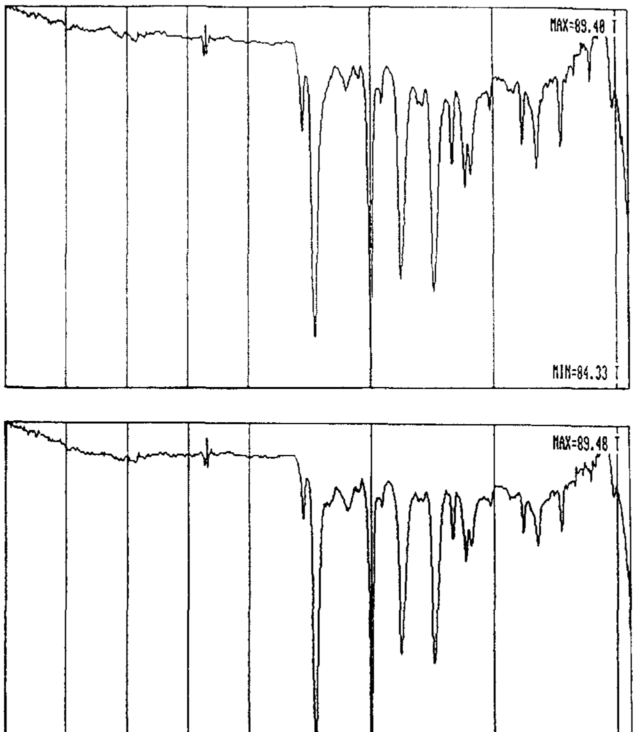

Figure 5 *FT*i.r. spectra of cured bulk polyimide (top) and cured polyimide after electrodeposition (bottom)

Table 1 Solid surface energy of uncoated T-650/35 carbon fibre

			Solid surface energy (mJ m^{-2})[a]					
			Geometric			Harmonic		
Sample	Perimeter (mm)	Diameter (μm)	γ^D	γ^P	γ^T	γ^D	γ^P	γ^T
1	0.0182	5.8	20.73	24.73	45.46	19.54	28.05	47.60
2	0.0178	5.7	30.08	21.43	51.51	26.13	26.61	52.74
3	0.0178	5.7	41.23	8.65	49.88	32.28	16.66	48.94
4	0.0178	5.7	16.12	32.19	48.31	17.14	33.00	50.14
5	0.0178	5.7	49.65	4.56	54.21	38.65	12.80	51.45
Average	0.0179	5.7	31.56	18.31	49.87	26.75	23.42	50.17
Std dev.	0.0002	0.0	13.95	11.47	3.29	8.90	8.39	2.02

[a] γ^D = solid dispersion component, γ^P = solid polar component, γ^T = total solid surface energy

Table 2 Solid surface energy of uncoated T-300 carbon fibre

			Solid surface energy (mJ m^{-2})[a]					
			Geometric			Harmonic		
Sample	Perimeter (mm)	Diameter (μm)	γ^D	γ^P	γ^T	γ^D	γ^P	γ^T
1	0.0178	5.7	42.46	13.89	56.35	34.18	21.81	55.99
2	0.0178	5.7	16.48	51.24	67.73	20.83	46.63	67.46
3	0.0178	5.7	24.92	36.39	61.31	25.21	37.19	62.41
4	0.0178	5.7	46.02	12.80	58.83	36.81	21.24	58.05
5	0.0178	5.7	19.23	32.13	51.37	19.67	33.29	52.96
Average	0.0178	5.7	29.82	29.29	59.12	27.34	32.03	59.37
Std dev.	0.0	0.0	13.57	16.20	6.06	7.78	10.75	5.68

[a] γ^D = solid dispersion component, γ^P = solid polar component, γ^T = total solid surface energy

Table 3 Solid surface energy of T-650/35 carbon fibre coated with polyamic acid PI2545: P/S ratio, 3.5/1; solid content, 1.0 wt%; TEA/COOH mole ratio, 1/1; current density, 50 mA; deposition time, 60 s

			Solid surface energy (mJ m^{-2})^a					
			Geometric			Harmonic		
Sample	Perimeter (mm)	Diameter (μm)	γ^D	γ^P	γ^T	γ^D	γ^P	γ^T
1	0.4770	151.8	35.99	3.46	39.45	28.81	9.96	38.76
2	0.4284	136.4	30.16	6.41	36.57	24.18	13.17	37.35
3	0.3827	121.8	20.32	12.52	32.84	17.48	18.36	35.84
4	0.3212	102.2	34.94	11.83	46.77	28.00	19.08	47.08
5	0.4074	129.7	29.27	5.78	35.05	23.60	12.37	35.97
Average	0.4033	128.4	30.14	8.00	38.14	24.41	14.59	39.00
Std dev.	0.0575	18.3	6.21	3.97	5.39	4.50	3.96	4.67

^{a} γ^D = solid dispersion component, γ^P = solid polar component, γ^T = total solid surface energy

Table 4 Solid surface energy of T-300 carbon fibre coated with polyamic acid PI2545: P/S ratio, 3.5/1; solid content, 1.0 wt%; TEA/COOH mole ratio, 1/1; current density, 50 mA; deposition time, 60 s

			Solid surface energy (mJ m^{-2})^a					
			Geometric			Harmonic		
Sample	Perimeter (mm)	Diameter (μm)	γ^D	γ^P	γ^T	γ^D	γ^P	γ^T
1	0.4236	134.8	55.30	4.49	59.80	43.20	13.30	56.50
2	0.3910	124.4	30.99	15.60	46.58	25.68	21.97	47.65
3	0.4289	136.5	27.16	9.45	36.61	22.11	16.08	38.19
4	0.3279	104.4	76.49	0.11	76.60	68.49	5.81	74.30
5	0.5657	180.1	41.37	2.90	44.26	32.90	9.59	42.50
Average	0.4274	136.0	46.26	6.51	52.77	38.48	13.35	51.83
Std dev.	0.0871	27.7	20.11	6.11	15.73	18.61	6.18	14.29

^{a} γ^D = solid dispersion component, γ^P = solid polar component, γ^T = total solid surface energy

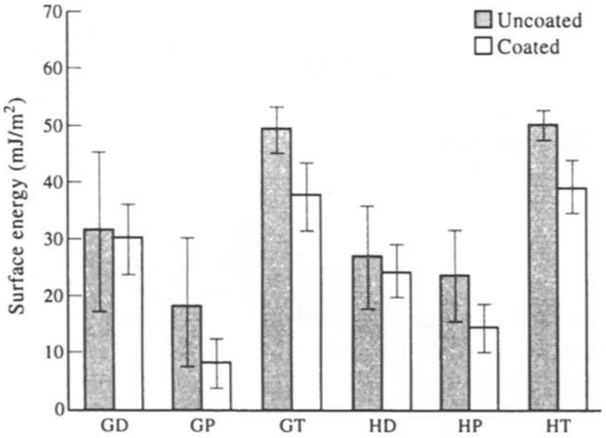

Figure 6 Comparison of surface energy of coated and uncoated T-650/35 carbon fibres: D = dispersive, P = polar, T = total; G = geometric mean method, H = harmonic mean method

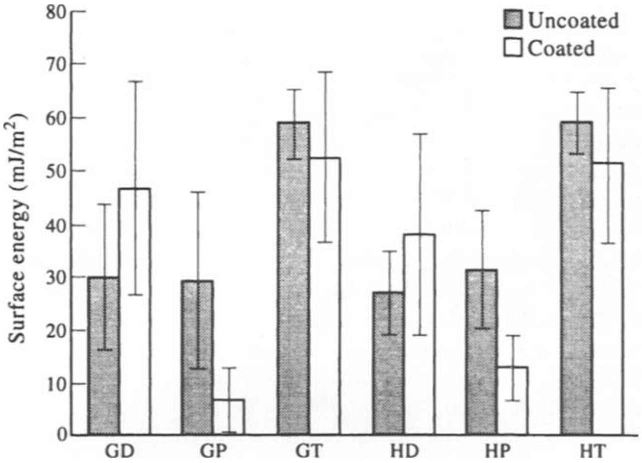

Figure 7 Comparison of surface energy of coated and uncoated T-300 carbon fibres: D = dispersive, P = polar, T = total; G = geometric mean method, H = harmonic mean method

surface. A significant difference was observed for the γ^T of the coated T-650/35 and T-300 fibre, even though both fibres were coated under the same conditions. Contrary to the behaviour of the non-coated fibres, the difference in γ^T between the coated T-650/35 and T-300 fibres lies mainly in their γ^D. The reason for this behaviour is not clear. It might be due to the interaction between the wetting medium (formamide) and the deposited polyamic acid film, or to the difference in the orientation of the polyamic acid chains on the carbon fibre surface.

The surface energies of T-650/35 and T-300 single fibres are compared in *Figures 6* and *7* respectively. The γ^D, γ^P and γ^T for both fibres decreased after electrodeposition. Note, however, that γ^D for T-300 fibre increased after electrodeposition. The average values of the surface energies for the coated T-650/35 single fibres may represent the surface properties of polyamic acid coatings. These values are very similar to the literature values for nylon 6,6 and polyester fibre[21]. The reason for

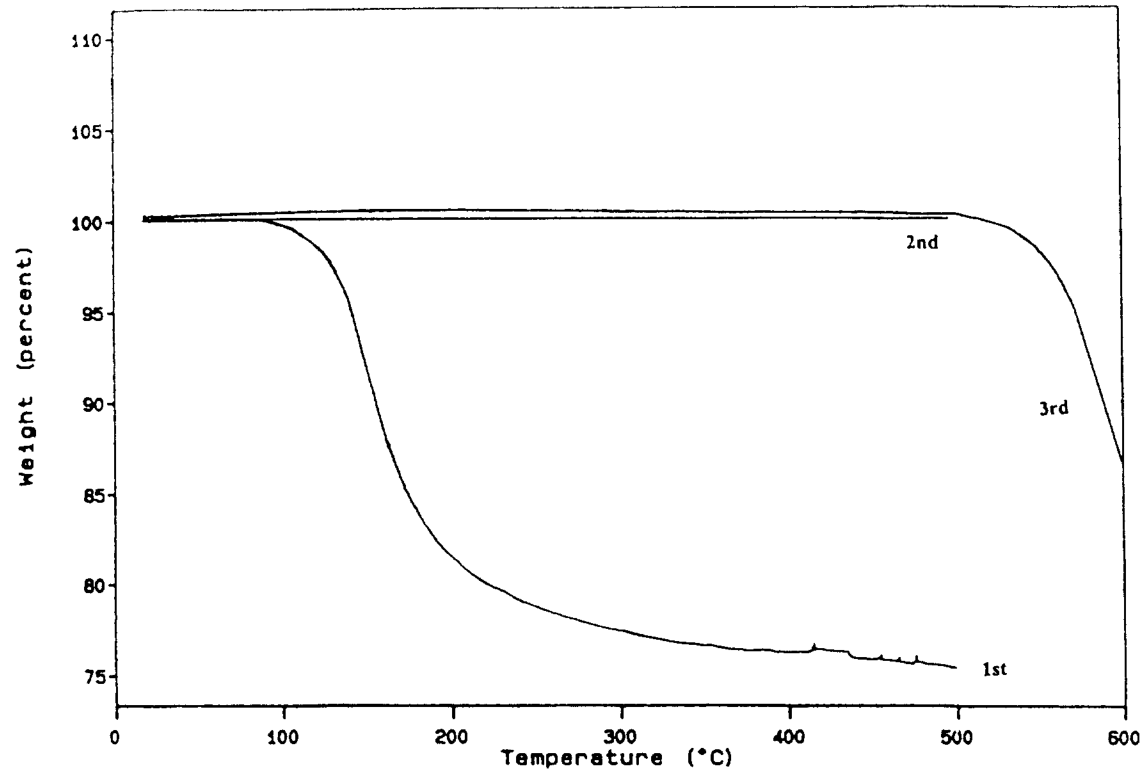

Figure 8 T.g.a. trace for electrodeposited polyimide film

the high value of γ^D for coated T-300 single fibre is not clear. Preliminary results suggest a dependence of coated fibre surface energy on the thickness of the coatings. The surface energy of fibres coated with very thin polyamic acid coatings (~0.01–0.1 μm) is believed to be about twice the value reported for fibres with very thick coatings (≥1 μm).

Thermal gravimetric analysis (t.g.a.). T.g.a. analysis was carried out three times consecutively for the same sample. In the first run, the sample was heated to 500°C. After cooling, the sample was re-heated to 500°C in the second run. In the third run, after cooling, the sample was further heated to 600°C. The t.g.a. thermograms of these runs are shown in *Figure 8*. About 25% weight loss was observed in the first run, occurring at about 140–200°C. This might be due to evaporation of the by-products of the imidization reaction (water) and the release of entrapped solvent. It is suggested that polyamic acid is completely converted to polyimide after thermal treatment at 200°C. We may recall that the *FT*i.r. spectra of the polyimide, cured at 200°C for 60 min, confirmed the disappearance of the N–H peak absorption at about 3400 cm^{-1} and the appearance of the imide carbonyl peak absorption at 1771 cm^{-1} (*Figures 4* and *5*), in agreement with the suggested complete conversion of polyamic acid into polyimide. No significant weight loss was observed in the second and third run until after about 540°C, where decomposition of the polyimide occurred. The t.g.a. results also demonstrate that the electrodeposited polyimide has excellent thermal stability and is therefore suitable for moderate to high temperature applications.

Conclusions

Electrodeposition of polyamic acid films onto carbon fibres has been studied with the aim of modifying the surface of the fibres. Electrodeposition was performed galvanostatically from emulsions, resulting in the formation of a smooth and uniform coating on the fibres. There was evidence that the freshly coated polyamic acid film was not completely insulating. The diameter of the coated single fibre was as high as 100 μm. The significance of this work is that a controlled thickness of polymer matrix can be applied directly onto a conductive substrate. This technique is especially very useful in the production of high resin content prepregs and composites.

Dynamic contact angle measurement is a valuable technique for assessing the surface properties of coated and non-coated fibres. The average values of the total surface energies, as well as their dispersive and polar components, for the uncoated T-650/35 and T-300 single fibres are in the range of the values reported for fibres modified by oxidative treatment. The average value of the polar component of the non-coated T-300 fibre remained slightly higher than that of the non-coated T-650/35 fibre. This confirms that the T-300 fibre has more polar chemical functional groups on its surface. The total surface energy and the polar component of the surface energies for both fibres, coated with very thick coatings of polyamic acid (~100 μm), were found to be slightly lower than those of the non-coated fibres. The surface energies of the coated fibres are comparable to the published values for nylon 6,6 and polyester fibres, indicating that the surface properties of the coated fibres are controlled mainly by the surface properties of the coatings.

*FT*i.r. study indicated that the polymer structure did not change during electrodeposition, thus demonstrating that a controlled polymer interphasial structure can be obtained by electrodeposition. Thermal analysis study suggested that the imidization of polyamic acid occurred around 140°C and completed at about 200°C. The cured polyimide has excellent thermal stability up to 540°C and is suitable for high temperature applications.

Acknowledgement

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